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Living Polymerization of Ethylene and Copolymerization of Ethylene/Methyl Acrylate Using "Sandwich" Diimine Palladium Catalysts

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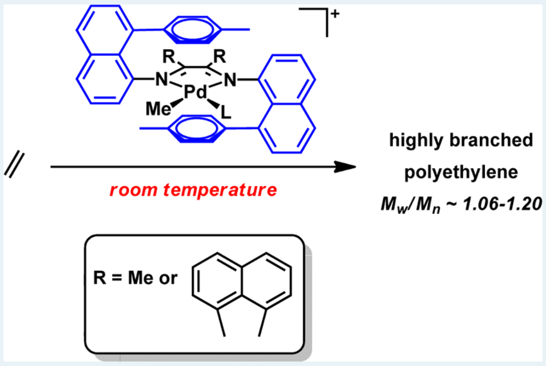
S *Supporting Information*

ABSTRACT: Cationic Pd(II) catalysts incorporating bulky 8-*p*-tolylnaphthyl substituted diimine ligands have been synthesized and investigated for ethylene polymerization and ethylene/methyl acrylate copolymerization. Homopolymerization of ethylene at room temperature resulted in branched polyethylene with narrow M_w/M_n values (ca. 1.1), indicative of a living polymerization. A mechanistic study revealed that the catalyst resting state was an alkyl olefin complex and that the turnover-limiting step was migratory insertion, thus the turnover frequency is independent of ethylene concentration. Copolymerization of ethylene and methyl acrylate (MA) was also achieved. MA incorporation was found to increase linearly with MA concentration, and copolymers with up to 14 mol % MA were prepared. Mechanistic studies revealed that acrylate insertion into a Pd−CH_3 bond occurs at −70 °C to yield a four-membered chelate, which isomerizes first to a five-membered chelate and then to a six-membered chelate. Barriers to migratory insertion of both the (diimine)$PdCH_3(C_2H_4)^+$ (19.2 kcal/mol) and (diimine)$PdCH_3(\eta^2\text{-}C_2H_3CO_2Me)^+$ (15.2 kcal/mol) were measured by low-temperature NMR kinetics.



KEYWORDS: *palladium, diimine, ethylene, living polymerization, methyl acrylate*

■ INTRODUCTION

Late transition metal polymerization catalysts employing modified bulky diimine ligands have received recent significant interest.[1,2] Catalysts that promote the living polymerization of ethylene and α-olefins are of interest because polymers with controlled molecular weight, end-group functionalities, and block structures can be prepared.[3] α-Diimine Ni and Pd complexes featuring bulky *ortho* N-aryl substituents are highly active olefin polymerization catalysts (Figure 1).[4] Catalysts based on Pd have been found to promote the living polymerization of ethylene at low temperatures and can be used to synthesize block polymers of ethylene and α-olefins.[5,6] Additionally, copolymerization of ethylene and polar monomers, such as methyl acrylate (MA), has been observed using diimine Pd catalysts.[7,8]

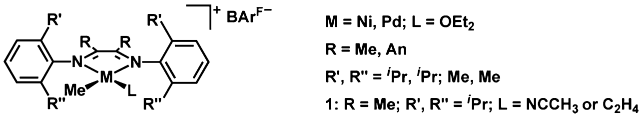


Figure 1. Previously reported α -diimine catalysts.

The nature of substituents R, R′, and R″ plays a large role in determining the molecular weight of the polymers.[9] Systematic variation of the aryl and diimine substituents revealed that the key to obtaining high molecular weight polymers is to incorporate bulky substituents that effectively block the axial positions of the square planar complexes, thereby preventing chain transfer.[10] Guan and co-workers developed cyclophane diimine Ni and Pd catalysts which have rigid bridging groups at the *ortho* N-aryl positions. Catalysts bearing the cyclic diimine ligand exhibit increased thermal stability in comparison to traditional diimine catalysts but produce polyethylene of lower M_n.[11] Interestingly, Pd cyclophane catalysts afford methyl acrylate and ethylene copolymers with significantly higher polar monomer incorporation than previously observed.[12]

A general catalytic cycle for ethylene polymerization has been proposed on the basis of mechanistic studies using traditional diimine Ni and Pd systems.[13−16] For Pd catalysts, the resting state is an alkyl olefin species. Therefore, the rate of polymerization is independent of ethylene pressure (Scheme 1). A unique feature of the diimine catalysts is migration of the metal center along the growing polymer chain, which is referred to as "chain walking" (Scheme 1). This process occurs via β-hydride elimination generating a Pd-hydride olefin species (B), followed by reinsertion with opposite regiochemistry to produce an agostic species. Coordination and insertion of ethylene results in a methyl branch (C). An additional chain-running step (D) followed by ethylene insertion yields an ethyl

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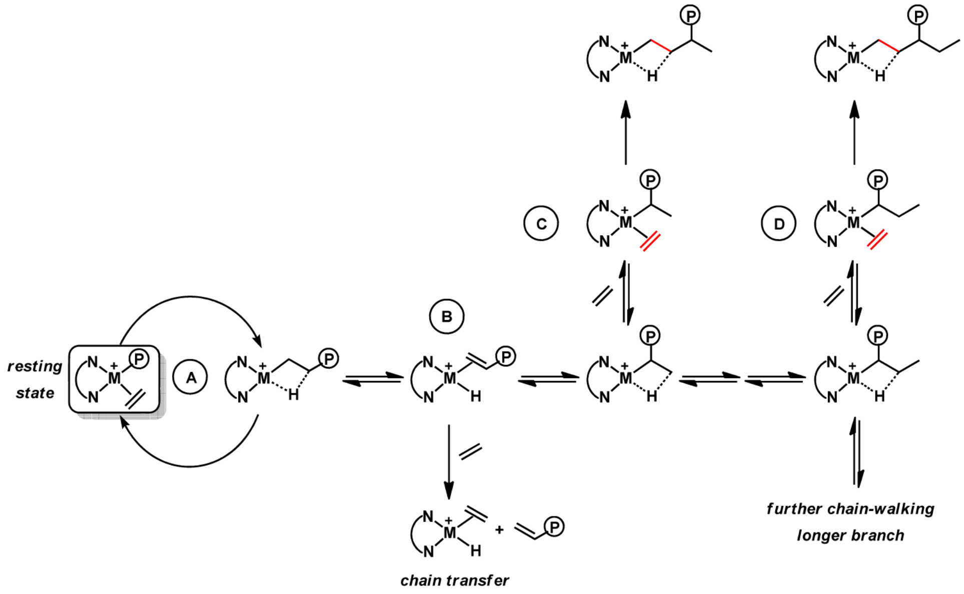
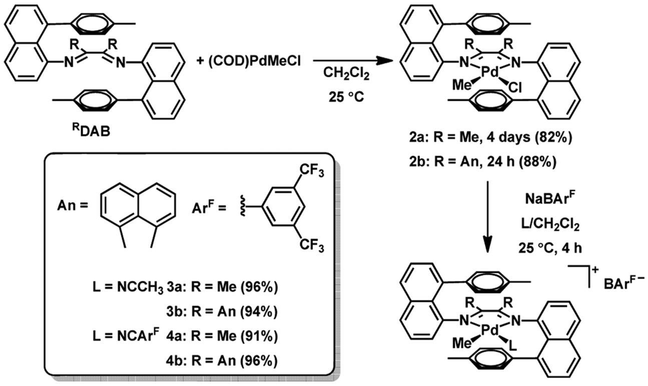
Scheme 1. Proposed Mechanism for Pd-Catalyzed Ethylene Polymerization



branch. Further chain-running results in longer branches. For Ni catalysts, the degree of branching can be controlled by temperature and/or ethylene pressure as trapping and insertion of ethylene is competitive with chain-walking. Reducing the steric bulk of the *ortho* substituents results in faster trapping by ethylene and reduced branching densities.

Recently, we reported ethylene polymerization using "sandwich" diimine Ni catalysts, which produced highly branched polyethylene at 70 °C.[17] Additionally, Coates, Daugulis, and co-workers have utilized these Ni catalysts and their derivatives in the polymerization of linear α-olefins to produce "chain-straightened" polymers with low branching densities.[18] It was envisioned that incorporation of the bulky 8-*p*-tolylnaphthylene substituents (Scheme 2) would decrease the rate of chain transfer relative to chain propagation. Although narrower M_w/M_n distributions were obtained, the turnover frequencies of these catalysts were 2–3 times slower than the traditional Ni catalysts. In order to better understand the effect of the "sandwich" diimine ligand and to further explore the potential of these catalysts, the Pd(II) analogues have been synthesized and explored for ethylene homopolymerization and copolymerization with methyl acrylate. The results from mechanistic studies are discussed herein and provide insight into such polymerizations.

Scheme 2. Synthesis of Pd(II) Complexes



■ RESULTS AND DISCUSSION

Synthesis of Pd Precatalysts. The syntheses of the diimine ligands used in this study have been previously reported.[17,19] Coordination of the "sandwich" diimine ligands to Pd proceeded smoothly via displacement of COD from (COD)PdMeCl to generate (^{R}DAB)PdMeCl (**2a**, R = Me; **2b** R = An) in high yields (Scheme 2). Complexes **2a** and **2b** were characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and X-ray crystallography. The ORTEP diagrams of these complexes are shown in Figures 2 and 3. As expected, both **2a** and **2b** exhibit square planar geometries about the Pd(II) center in the solid state. The two tolyl rings effectively cap the axial sites at the Pd center. Accurate determination of the Pd-CH$_3$ and Pd–Cl bond lengths in these systems is precluded due to the disorder of these ligands over the two sites.

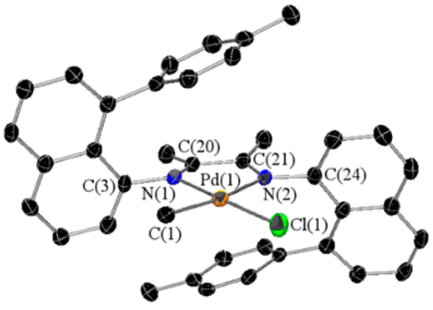


Figure 2. ORTEP diagram of (^{Me}DAB)PdMeCl (**2a**) (thermal ellipsoids at 50% probability, H atoms omitted for clarity). The Cl(1) and C(1) are disordered 90:10 over the two sites. Select bond distances (Å) and angles (deg): Pd(1)–Cl(1) = 2.2907(9), Pd(1)–C(1) = 2.21(4), Pd(1)–N(1) = 2.051(2), Pd(1)–N(2) = 2.142(2), N(1)–C(3) = 1.439(3), N(2)–C(24) = 1.432(3), N(1)–C(20) = 1.290(3), N(2)–C(21) = 1.283(3), N(1)–Pd(1)–N(2) = 77.39, N(1)–Pd(1)–C(1) = 93.04(16), N(2)–Pd(1)–C(1) = 170.31(15).

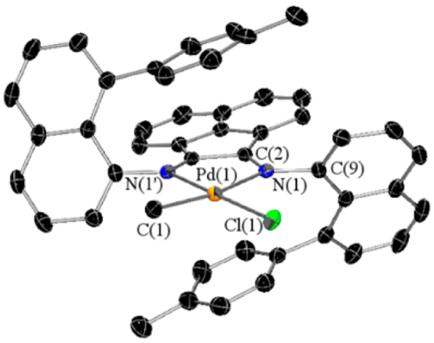
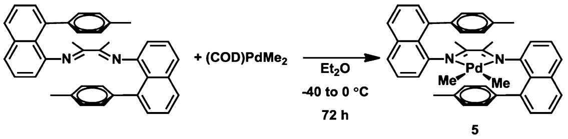


Figure 3. ORTEP diagram of (^{An}DAB)PdMeCl (**2b**) (thermal ellipsoids at 50% probability, H atoms omitted for clarity). The Cl(1) and C(1) atoms are disordered 50:50 over the two sites. Select bond distances (Å) and angles (deg): Pd(1)−Cl(1) = 2.2799(16), Pd(1)−C(1) = 2.054(10), Pd(1)−N(1) = 2.11279(17), Pd(1)-N(1′) = 2.1128(17), N(1)−C(9) = 1.433(2), N(1)−C(2) = 1.283(3), N(1)−Pd(1)−Cl(1) = 97.93(6), N(1′)-Pd(1)−N(1) = 79.66(9), C(1)−Pd(1)−N(1) = 92.3(3).

Halide abstraction from **2a**,**b** using 1 equiv of NaBAr^F (Ar^F = 3,5-$C_6H_3(CF_3)_2$) in the presence of acetonitrile or 3,5-(trifluoromethyl)benzonitrile resulted in the formation of the corresponding cationic complexes [(^{R}DAB)Pd(Me)L][BAr^F] (**3**; L = $NCCH_3$ and **4**; L = NCAr^F) in high yields (Scheme 2). The nitrile precatalysts were characterized using ^{1}H and ^{13}C NMR spectroscopy and elemental analysis.

Although nitrile complexes are amenable to conducting preparative scale polymerization experiments, species with more labile ligands are required to conduct low-temperature mechanistic studies. Complexes of this nature can easily be obtained by the addition of 1 equiv of $H(OEt_2)_2BAr^F$ to (diimine)$PdMe_2$ complexes at low temperature to generate CH_4 and a cationic (diimine)Pd(Me)OEt_2^+ species.[10] The labile ether ligand is readily displaced by ethylene making these complexes attractive for NMR studies. For the mechanistic studies discussed below, (^{Me}DAB)Pd(Me)$_2$ (**5**) was prepared in 83% yield by treating (COD)$PdMe_2$ with ^{Me}DAB at 0 °C over the course of 72 h (eq 1).



(1)

Complex **5** was characterized by ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis. The C_2-symmetric nature of **5** is evident in the ^{1}H NMR spectrum as only one signal is observed for the two methyl substituents on the diimine backbone. The Pd−Me signal is observed at −0.35 ppm integrating to six protons relative to the tolyl and imine Me substituents at 2.35 and 1.15 ppm, respectively, each integrating to six protons.

Ethylene Polymerization. Polymerization of ethylene using precatalysts **3** and **4** was initially explored at room temperature in CH_2Cl_2 solutions with 16 h reaction times. Table 1 summarizes the polymerization data obtained using these catalysts at varying ethylene pressures. The M_n and M_w values were obtained using high temperature GPC and polyethylene standards. The degree of branching was determined using ^{1}H NMR spectroscopy.[20] As expected little variation in turnover frequencies (TOFs) were observed at different ethylene pressures (8−27.2 atm). Additionally, reactions conducted in the presence of 10 equiv of acetonitrile using **3a** resulted in only a slightly lower TOF (146 vs 183 h^{-1} under 13.6 atm ethylene). This result suggests that under these conditions only a small fraction (ca. 20%) of the catalyst "rests" as the nitrile complex and that in the absence of added nitrile the resting state(s) are almost exclusively alkyl ethylene complexes (Scheme 1). These results are consistent with previous observations made in the standard diimine system **1**. Catalysts bearing the dimethyl backbone, **3a** and **4a**, exhibit TOFs in the range of 170−200 h^{-1} and are more active than the acenaphthylene derivatives **3b** and **4b** which show TOFs in the range of 60−75 h^{-1}. The polyethylenes obtained under these conditions (16 h, 25 °C) using either **3a** or **4a** have similar M_n values (50−60 kg/mol), and these values are significantly higher than those for **3b** and **4b** (15−25 kg/mol) at all ethylene pressures (Table 1, entries 2−7 vs entries 8−13). This trend in reactivity is consistent with previous observations.[6,8] In comparison to "standard" diimine catalyst **1**, the productivities of the "sandwich" catalysts **3a** and **4a** are approximately 10 times lower (entry 1 vs entries 2−7). The significantly slower rate of insertion observed for **3a** accounts for this difference and is discussed vide infra.

The molecular weight distributions are dependent on the nature of R (R = Me or An; Scheme 2). The M_w/M_n values observed for experiments using **3a** and **4a** range from 1.06 to 1.10 (Table 1; entries 2−7), fully consistent with living polymerization. These results suggest that longer reaction times should result in polyethylene with a higher M_n. Indeed when polymerization runs were conducted for 24 and 48 h time periods using catalyst **3a**, polyethylene of higher M_n was obtained (Table 2; entries 2−3). The M_n at 48 h is slightly lower than expected, which likely is the result of some catalyst decomposition. Consistent with this contention is the fact that the computed average TOF has dropped and the M_w/M_n is slightly elevated (1.22) in comparison to the 16 and 24 h reactions.

The TOF was calculated based on the moles of catalyst and the yield of polymer produced per hour. Assuming living behavior, the M_n for a run may be calculated using the TOF. Using this method for entry 1, Table 2, the M_n value is calculated to be approximately 82 K, which is 1.5 times greater than the M_n determined using polyethylene standards. Thus, the M_n values reported in Tables 1 and 2 likely underestimate the true M_n of the polymers reported here.

In experiments with catalysts **3b** and **4b**, bearing the acenaphthylene backbone, the formation of Pd black was observed. Only slightly higher M_w/M_n values were observed for **3b** and **4b** (Table 1; entries 8−13) in comparison to catalysts **3a** and **4a**. It appears that for **3b** and **4b** catalyst decomposition broadens M_w/M_n. Ethylene polymerization reactions conducted at 40 °C were slightly more productive (Table 2, entries 4−6). Despite this marginal increase in polyethylene yield, significantly higher M_w/M_n values in comparison to room temperature reactions were observed indicating an increase in the rate of chain transfer relative to propagation at 40 °C.

Typically the degree of branching in Pd diimine-catalyzed polymerization reactions is independent of pressure. Polyethylene produced using catalysts **3a** and **4a** exhibits 115−117 branches per 1000 carbons. In comparison, catalysts **3b** and **4b** bearing the acenaphthylene backbone yielded polymers with slightly lower branching densities (102−107 branches/1000C, Table 1). Runs at longer times generated polymers with similar

Table 1. Effect of Catalyst and Pressure on Ethylene Polymerization

entry	cat[a]	*P* (atm)	yield (g)	M_n[b] ($\times 10^{-3}$)	M_w/M_n	TOF (h^{-1})	productivity[c]	branches[d] (per 1000 carbons)
1	**1**	13.6	8.77	138	2.16	1960	877	98
2	**3a**	8	0.775	49.2	1.10	173	77.5	115
3	**3a**	13.6	0.820	54.6	1.06	183	82.0	117
4	**3a**	27.2	0.733	49.3	1.10	164	73.3	115
5	**4a**	8	0.754	48.4	1.08	168	75.4	115
6	**4a**	13.6	0.906	63.4	1.09	202	90.6	116
7	**4a**	27.2	0.878	63.8	1.10	196	87.8	111
8	**3b**	8	0.350	16.2	1.20	77	34.7	107
9	**3b**	13.6	0.352	18.4	1.18	78	35.2	105
10	**3b**	27.2	0.338	24.2	1.17	75	33.8	104
11	**4b**	8	0.250	18.9	1.12	56	25.0	105
12	**4b**	13.6	0.246	22.6	1.18	55	24.6	103
13	**4b**	27.2	0.250	23.7	1.09	56	25.0	102

[a] Conditions: 0.010 mmol catalyst loading, 40 mL of CH_2Cl_2, 25 °C, 16 h. [b] Molecular weight was determined by GPC in trichlorobenzene at 150 °C using polyethylene standards. [c] kg of polymer per mole of catalyst. [d] Branching numbers were determined using ^1H NMR spectroscopy in $CDCl_3$.

Table 2. Effect of Time and Temperature on Ethylene Polymerization

entry	cat[a]	time (h)	temp (°C)	yield (g)	M_n[b] ($\times 10^{-3}$)	M_w/M_n	TOF (h^{-1})	productivity[c]	branches[d] (per 1000 carbons)
1	**3a**	16	25	0.820	54.6	1.06	183	82.0	117
2	**3a**	24	25	1.33	86.0	1.12	198	133	112
3	**3a**	48	25	2.09	153	1.22	155	209	117
4	**3a**	16	40	0.913	57.1	2.01	203	91.3	115
5	**4a**	16	40	1.05	62.5	2.11	237	105	115
6	**3b**	16	40	0.504	17.9	1.67	112	50.4	111

[a] Conditions: 0.010 mmol catalyst loading, 13.6 atm C_2H_4, 40 mL of CH_2Cl_2. [b] Molecular weight was determined by GPC in trichlorobenzene at 150 °C using polyethylene standards. [c] kg of polymer per mole of catalyst. [d] Branching numbers were determined using ^1H NMR spectroscopy in $CDCl_3$.

branching numbers (Table 2). In comparison to standard catalyst **1** the polymers produced using "sandwich" diimine catalysts have a higher degree of branching.

Analysis of the polyethylene microstructure by ^{13}C NMR spectroscopy revealed the presence of a "branch on branch" moiety, specifically a *sec*-butyl branch (Figure 4, Table 3). In the ^{13}C NMR spectrum of the polyethylene reported in entry 3, Table 1, resonances at 12.17 and 19.87 ppm confirm the formation of *sec*-butyl branches. Hyperbranching of this nature has been observed in polyethylene generated from catalyst **1** and in this case the density of *sec*-butyl branches was dependent on ethylene pressure.[21] Lowering the ethylene pressure from 13.6 to 8 atm did not result in noticeably different polymer microstructure, which suggests that hyperbranching in the "sandwich" Pd systems is independent of ethylene pressure in this range. A comparison of the degree of "branch on branch" structures in the polyethylene made in entries 6, 9, and 12 of Table 1 demonstrates that the nature of the diimine backbone does not have a large impact on branching density.

Copolymerization of Methyl Acrylate and Ethylene. The standard diimine catalyst **1** has been shown to copolymerize ethylene and methyl acrylate.[7,8] Mechanistic studies established that exposure of the ether adduct of **1** to MA at low temperatures resulted in insertion of MA in a 2,1 fashion to generate first a four-membered chelate followed by rearrangement to a five-membered chelate and ultimately conversion to the most thermodynamically stable six-membered chelate isomer at higher temperatures. The analogous six-membered chelate complex of sandwich catalyst **3a**, $[(^{Me}DAB)Pd(CH_2)_3C(O)OMe][BAr^F]$ (**3c**), was generated via halide abstraction from **2a** with $NaBAr^F$ in the presence of 1 equiv of MA (eq 2). The presence of the six-membered chelate ring was confirmed by ^1H and ^{13}C NMR spectroscopy and by comparison to the analogous chelate derived from **1**. A minor

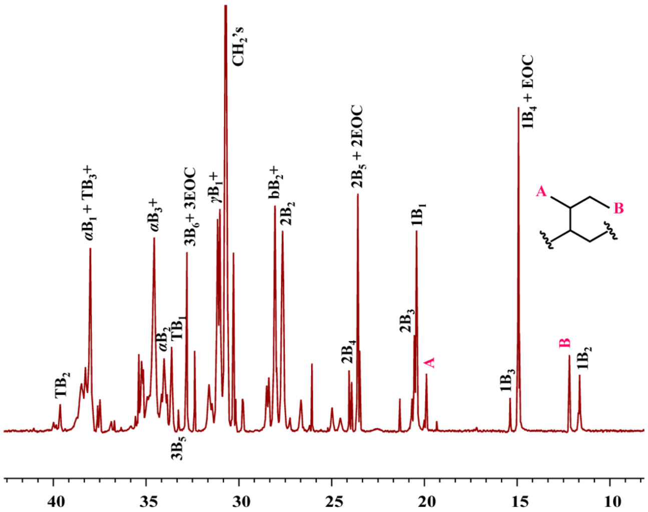
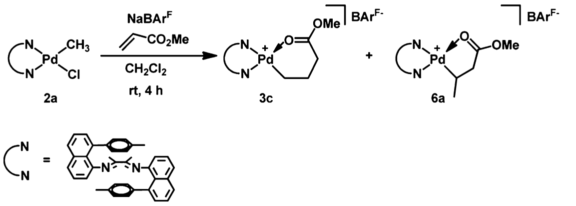


Figure 4. ^{13}C NMR spectrum (600 MHz) of polyethylene from Table 1, entry 3. The polymer was dissolved in 1,2-dichlorobenzene with 0.05 M $Cr(acac)_2$, referenced to the triplet resonance at 127.9 ppm for DCB. The resonances labeled A and B correspond to the methyl and ethyl groups of the *sec*-butyl ended branch. Guide for labels: for xBy, By is a branch of length y (y = 1−5) carbons and x is the carbon being discussed. The methyl group at the end of branch is numbered 1. xBy+ refers to branches of y length and longer. Replacing x with T indicates the methine carbon of that branch. Methylenes in the backbone are labeled with Greek letters (such as *α* or *γ*) which denote how far each methylene is from a branch point. EOC is end of chain and 2EOC refers to the first CH_2 group from the end of chain.[21]

Table 3. Number of Polyethylene "Branch on Branch" Structures

catalyst	*P* (atm)	*sec*-butyl branches (per 1000 carbons)
1	13.6	7.6
3a	13.6	7.8
3a	8	8.1
4a	13.6	8.6
4a	8	8.5
3b	13.6	6.7
4b	13.6	8.5



(2)

product was also observed in the ^{1}H NMR spectrum of **3c** and assigned as the five-membered chelate [(^{Me}DAB)PdCH(Me)-$CH_2C(O)OMe$][BAr^F] (**6a**) (see below for additional details).

Copolymerizations of ethylene and MA were investigated using both **3a** and the chelate **3c**. Initial experiments were conducted using **3a** under 6 atm of ethylene and in 2.5 M MA solutions at 25 °C for 16.5 h. In the ^{1}H NMR spectrum of the resulting polymeric material, multiplets present at 2.30 and 1.60 ppm were indicative of MA−ethylene copolymer formation. These resonances are attributed to the MA methylene groups and are similar to those reported for copolymers produced using the standard diimine system.[8] Additional multiplets were observed in the same spectrum at 2.30, 1.93, 1.68, and 1.53 ppm. These resonances were indicative of the formation of MA homopolymer.[22] Analysis of the material by GPC confirmed the presence of two distinct polymers as two peaks were observed; one at high M_n (48×10^4 g/mol; $M_w/M_n = 1.15$) and a second peak at a significantly lower M_n (60×10^3 g/mol; $M_w/M_n = 1.16$). These results are in contrast to the standard catalyst **1**, where no MA homopolymer was present in the copolymer.[23] In a separate experiment, MA could be polymerized by **3a** at 25 °C in CH_2Cl_2 (Table 4, entry 2) resulting in a high M_n polymer, which suggests that in the initial copolymerization experiments the peak at high M_n corresponds to MA homopolymer.[24]

Homopolymerization of MA by **3a** may proceed by a radical mechanism or through MA coordination and insertion. A radical mechanism is typically invoked in acrylate homopolymerizations by Pd catalysts,[25] although an insertion mechanism is possible.[22] In order to distinguish between these possibilities, the polymerization of MA by **3a** was conducted in the presence of radical inhibitors. Novak and co-workers have shown that galvinoxyl is an effective inhibitor of Pd-catalyzed MA homopolymerization.[26] Indeed, when 5 equiv of galvinoxyl were used in reactions of MA with **3a**, no homopolymer was observed suggesting a radical mechanism for formation of these polymers.[27]

Copolymerization experiments conducted in the presence of galvinoxyl gave exclusively MA−ethylene copolymer (Table 4, entries 3−9). Catalysts **3a** and **3c** exhibit decreased activity in comparison to traditional catalyst **1**, whereas the degree of MA incorporation under the same conditions is similar in both systems. Higher branching numbers, as assessed by ^{1}H NMR spectroscopy, were observed for copolymers produced using catalysts **3a** and **3c** (111−121 branches/1000 carbons vs 97−105 branches for the traditional diimine system). The mole percent MA incorporation increases linearly with the concentration of MA. As MA incorporation increases, lower copolymer yields are obtained as a result of decreasing ethylene turnovers (entries 3−6 and 8−9, Table 4). Consistent with this observation, M_n also decreases with higher MA incorporation. Raising the ethylene pressure from 8 to 13.6 atm (entry 7) increases the ethylene turnovers and coincides with a decrease in MA incorporation. The low MA content can be attributed to the higher binding affinity of ethylene; furthermore, the overall lower productivity of copolymerization relative to homopolymerization (ethylene) is likely due to formation of a stable chelate resting state and the unfavorable equilibrium between the chelate and the alkyl olefin complex necessary for ethylene insertion. Both of these phenomena have been observed in the standard diimine system.[8]

MECHANISTIC STUDIES

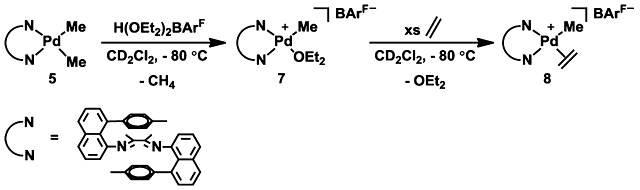
Ethylene Migratory Insertion. The rate of ethylene insertion into the Pd−Me bond of [(^{Me}DAB)Pd(Me)(C_2H_4)]-[BAr^F] (**8**) was examined at low temperatures using ^{1}H NMR spectroscopy. Complex **8** was generated from ether complex **7** as shown in Scheme 3. Complex **7** was generated in quantitative yields by the addition of 1.1 equiv of H-

Table 4. Effect of Reaction Conditions on MA−Ethylene Copolymerization

entry	cat[a]	[MA] (M)	*P* (atm)	polymer yield (g)	MA incorp. (%)	TON MA	TON E	M_n[b] (× 10^{-3})	M_w/M_n	branches (per 1000 carbons[c])
1	**3a**	-	13.6	0.820	-	-	2930	54.6	1.06	117
2[d]	**3a**	2.5	-	0.225	-	260	-	307[e]	1.59	-
3	**3a**	0.6	6	0.525	1.7	31	1780	29.6	1.21	114
4	**3a**	1.2	6	0.357	3.7	44	1140	28.1	1.17	115
5	**3a**	2.5	6	0.221	6.3	42	610	14.0	1.16	114
6	**3a**	5.0	6	0.147	13.8	56	350	4.7	1.45	121
7	**3a**	5.0	13.8	0.183	5.4	32	560	13.1	1.24	124
8	**3c**	1.2	6	0.30	4.2	43	960	22.6	1.22	114
9	**3c**	2.5	6	0.20	7.0	44	580	13.6	1.25	114
10	**3c**	-	8	0.74	-	-	2650	57.2	1.21	113
11	**3c**	-	13.8	0.77	-	-	2770	63.7	1.17	111

[a] Conditions: 0.010 mmol catalyst loading, 0.05 mmol galvinoxyl, total volume of CH_2Cl_2 and MA: 45 mL, 25 °C, 16.5 h. [b] Molecular weight was determined by GPC in trichlorobenzene at 150 °C using polyethylene standards. [c] Branching numbers were determined using ^{1}H NMR spectroscopy in $CDCl_3$. [d] Galvinoxyl was not used in this reaction. [e] Molecular weight was determined by GPC in THF using polystyrene standards.

Scheme 3. Generation of Cationic Pd Complexes



(OEt$_2$)$_2$BAr^F to **5** in CD$_2$Cl$_2$ solutions at −80 °C. In the ^{1}H NMR spectrum, the downfield shift from −0.31 to 0.15 ppm for the remaining methyl ligand concomitant with formation of CH$_4$ was indicative of protonolysis of a Pd−Me bond. Upon exposure of a solution of **7** to ca. 1 equiv of ethylene [(^{Me}DABPd(Me)(C$_2$H$_4$)][BAr^F] (**8**) is formed (Scheme 3). At −40 °C, two broad signals at 3.97 and 3.85 ppm are observed for coordinated ethylene together with a Pd−Me resonance at 0.11 ppm.

For mechanistic studies, complex **8** was generated in situ at −80 °C and used immediately. The initial insertion of ethylene exhibits first-order kinetics and was monitored at −25 °C by following the disappearance of the Pd−Me signal at 0.04 ppm. The rate for subsequent insertions is zero-order in ethylene and was determined from the turnover frequency based on the decreasing C$_2$H$_4$ peak at 5.43 ppm in the ^{1}H NMR spectrum. Rate constants k_1 and k_{sub} at −25 °C along with free energies of activation are summarized in Table 5. Similar values determined at −30 °C for standard system **1** reported previously are also summarized in Table 5.[14]

Table 5. Kinetic Data for Ethylene Migratory Insertion

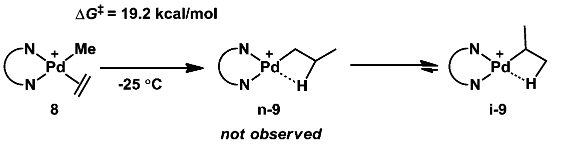
	first insertion		subsequent insertions	
catalyst	k_1 ($x10^3$ s^{-1})	$\Delta G_1^‡$ (kcal/mol)	k_{sub} ($x10^5$ s^{-1})	$\Delta G_{sub}^‡$ (kcal/mol)
1^a −30 °C	1.7	17.2	340	16.9
8 −25 °C	0.12	19.2	9.8	19.4

^{a}ref 14.

Comparison of k_{sub} for catalysts **1** and **8** confirms the significantly higher activity for the traditional diimine system, which is roughly an order of magnitude higher than that of the "sandwich" diimine system. The migratory insertion rates also agree with bulk polymerization experiments where the M_n of the polyethylene obtained using catalyst **1** is an order of magnitude larger than for **8** under identical reaction conditions. Rate constants for the first insertion of **8** were obtained over a temperature range of 25 °C (−25 to 0 °C) and used to generate an Eyring plot which provided $\Delta H^‡ = 20.0 \pm 0.2$ kcal/mol and $\Delta S^‡ = 3.1 \pm 0.1$ eu. A near zero value of $\Delta S^‡$ is consistent with an intramolecular rearrangement (migratory insertion).

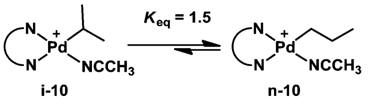
Alkyl Intermediates. Alkyl branches are formed by migration of the Pd along the growing polymer chain by facile *β*-hydride elimination and reinsertion steps. Following insertion of ethylene into a Pd-alkyl bond, elimination can occur to generate an olefin hydride complex. The coordinated olefin may then reinsert with opposite regioselectivity to give a new Pd-alkyl complex (Scheme 1). Insertion of ethylene into the new Pd-carbon bond leads to generation of a methyl branch. Longer branches can be introduced following additional chain running and reinsertion events. Earlier mechanistic studies on the standard system **1** showed that ethylene coordination was reversible and that, in contrast to the Ni analogues, Pd could migrate over a large number of carbon centers. This feature results in branching densities that are independent of ethylene pressure as is also observed for the systems studied here (Table 1).[15a]

Alkyl intermediates can be observed using low temperature NMR spectroscopy and are useful for probing the mechanism of branch formation. The addition of 1 equiv of ethylene to alkyl ether complex **7** in CDCl$_2$F leads to clean conversion to **8**. Migratory insertion occurs above −30 °C, resulting in a species which exhibits broad ^{1}H NMR signals suggestive of fluxional behavior (ether does not recoordinate to this complex). The static ^{1}H NMR spectrum could be obtained at −110 °C and supports assignment of this species as the *β*-agostic isopropyl species (**i-9**; eq 3), which must arise from isomerization of the *n*-propyl agostic species, **n-9**. The agostic proton of **i-9** appears as a triplet at −8.69 ppm with a $^2J_{HH}$ = 16.2 Hz. This splitting pattern is consistent with a *β*-agostic isopropyl species. A similar *β*-agostic proton signal with a geminal coupling constant of 17 Hz has been reported in the standard Pd system below −110 °C.[14] The remaining ^{1}H NMR resonances for **i-9** were located using COSY and 2D NOESY spectroscopy. The methine proton is observed at 1.86 ppm and the nonagostic methyl group appears as a doublet at −0.62 ppm ($^3J_{HH}$ = 5.8 Hz). The remaining two protons of the agostic methyl group appear as broad peaks at 0.58 and 0.76 ppm. The *n*-propyl isomer, **n-9**, was not observed at this temperature.



(3)

Upon the addition of 2 equiv of acetonitrile to a CDCl$_2$F solution of the agostic species at 0 °C, both the *n*-propyl and isopropyl isomers were observed (eq 4). Both **n-10** and **i-10** were characterized using 1D and 2D ^{1}H NMR spectroscopy. The major isomer, **n-10** was clearly identified by the presence of a triplet at 0.22 ppm and two broad multiplets at 0.60 and 0.76 ppm corresponding to the methylene protons. Two doublets at 0.27 and 0.36 ppm and a broad signal at 1.18 ppm were indicative of the isopropyl ligand of **i-10**. The equilibrium constant, *K*eq, for interconversion of **n-10**/**i-10** is 1.5 at 0 °C. Consistent with observations on the standard system,[14] the alkyl agostic species favors the branched isopropyl structure **i-9**, while trapping with a ligand L (in this case NCCH$_3$) leads to an equilibrium favoring the linear *n*-propyl species. These observations are consistent with DFT studies on system **1**.[28]



(4)

Chain Transfer. The living nature of these sandwich catalysts indicates that the rate of chain transfer is much, much lower than the rate of chain propagation. In comparison to the rates of migratory insertion in cationic diimine Pd(II) complexes, the rates of chain transfer are quite sensitive to substituents and decrease dramatically with increases in axial bulk.[14] One way to assess axial shielding is to compare the rates of associative exchange of ligands in these sites. For standard complex **1**, L = C$_2$H$_4$, the second-order rate constant for

Table 6. Rate Constants for Ethylene Exchange

complex	k_{obs1} (s^{-1}) (10 equiv C_2H_4)	k_{obs1} (s^{-1}) (20 equiv C_2H_4)	k_{obs2} (M^{-1} s^{-1})
8 (−50 °C)	4.0 (±0.4) × 10^{-5}	8.0 (±2.0) × 10^{-5}	2.4(±0.1) × 10^{-4}
1 (−85 °C)[a]	-	-	45

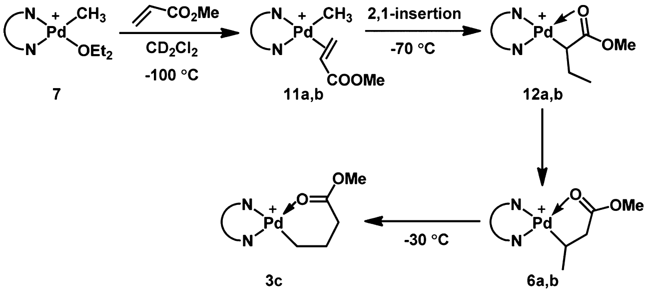
[a] ref 14.

associative exchange of bound ethylene with free ethylene measured by NMR line broadening was determined to be 45 M^{-1} s^{-1} at −85 °C, a rate far slower than the rate of exchange in (phen)Pd(CH_3)(C_2H_4)$^+$, which possesses no steric bulk in the axial sites.[29]

To compare these sandwich catalysts to the standard system **1**, the rate of exchange of ethylene in **8** with free ethylene was examined. Surprisingly, the exchange rate could not be determined by NMR line-broadening experiments as migratory insertion occurs prior to any line broadening of the ethylene signals. We thus turned to deuterium labeling experiments. Complex **8-*d*$_4$** was generated in situ from **7** and ethylene-d_4 in CD_2Cl_2. An excess of unlabeled ethylene was added (10 or 20 equiv) and the rate of incorporation of unlabeled ethylene into **8** was monitored by ^{1}H NMR spectroscopy at −50 °C. Results are summarized in Table 6. The exchange rate is proportional to ethylene concentration indicating an associative mechanism for exchange. Remarkably, the rate of exchange is a factor of almost 2 × 10^5 *slower* for **8** relative to **1** at a temperature 35 degrees higher! The difference in free energies of activation is ca. 6 kcal/mol. These results clearly demonstrate that axial shielding by the capping tolyl groups in **8** is far more effective than shielding achieved by the *ortho*-isopropyl groups in **1**.[30]

Migratory Insertion of Methyl Acrylate. A summary of observations concerning the migratory insertion of MA is contained in Scheme 4. Displacement of the OEt_2 ligand from complex **7** by MA at −100 °C in CD_2Cl_2 resulted in the formation of two isomers of the η^2-methyl acrylate complex [(^{Me}DAB)PdMe(CH_2)$_2$C(O)OMe][BAr^F] (**11a,b**) in a 90:10 ratio. Olefinic resonances for the major isomer (**11a**) were observed at 4.04 (d, J_{HH} = 8.5 Hz), 4.14 (dd, $^3J_{HH}$ = 14.5 Hz, $^3J_{HH}$ = 9.0 Hz), and 4.89 ppm (d, $^3J_{HH}$ = 14.7 Hz).[31] Resonances attributable to the minor isomer (**11b**) were observed at 5.61 (dd, $^3J_{HH}$ = 17.7 Hz, $^3J_{HH}$ = 10.6 Hz), 5.77 (d, $^3J_{HH}$ = 10.6 Hz), and 5.99 ppm (d, $^3J_{HH}$ = 16.7 Hz). Migratory insertion of MA in **11a** was observed at −70 °C by monitoring the disappearance of the MA olefinic resonance at 4.89 ppm. First-order kinetics were observed with k_{ins} = 2.0 × 10^{-4} s^{-1} ($\Delta G^\ddagger$ = 15.2 kcal/mol). This rate is similar to that determined for the standard system **1** (k_{ins} = 3.3 × 10^{-4} s^{-1} at −70 °C).[8]

Scheme 4. Formation of Six-Membered Chelate Species 3c



As for system **1**, migratory insertion occurs in a 2,1 fashion, but the case here is complicated by the fact that the diimine ligand possesses C_2 symmetry. Thus, rather than formation of a single four-membered chelate as observed for system **1**, two diastereomeric four-membered chelates, [(^{Me}DAB)Pd(CHEtC(O)OMe][BAr^F] (**12a,b**), are formed in a ca. 1:1.5 ratio. The clearest evidence for these chelates is the observation of two methyl triplets (J_{HH} = 6.9 Hz) at 0.25 and 0.46 ppm in the ^{1}H NMR spectrum (−70 °C). Rearrangement of the four-membered chelates, **12a,b**, to two diastereomeric five-membered chelates, **6a,b** also occurred at −70 °C, albeit at a much slower rate than migratory insertion. In the ^{1}H NMR spectrum of **6a,b**, the formation of diastereomers was indicated by the presence of two methyl doublets at −0.03 (**6a**) and −0.17 (**6b**) ppm ($^3J_{HH}$ = 7.1 Hz and $^3J_{HH}$ = 7.1 Hz, respectively) in a 1:1 ratio.

Isomerization of diastereomers **6a,b** to the six-membered chelate **3c** occurred at −30 °C. Conversion of one diastereomer (exhibiting the doublet at −0.17 ppm) proceeded at a somewhat faster rate than conversion of the other diastereomer (doublet at −0.03 ppm). The formation of **3c** was clearly indicated by the presence of two multiplets at 0.45 and 0.63 ppm assigned to the two β-methylene protons of the chelate.[8] A doublet at 0.07 ppm and a multiplet at 1.03 ppm, which integrated in a 3:1 ratio, confirmed that a small fraction of the diastereomer exhibiting a methyl doublet at −0.07 ppm (**6a**) persists at long times, indicating it is present in equilibrium with **3c**.

The summary of the behavior of the η^2 acrylate complexes **6a,b** is shown in Scheme 4. The stepwise formation of the 4-, 5- and six-membered chelate complexes and their approximate rates of formation closely parallels the same chemistry observed in system **1**. The primary difference here is that owing to the C_2 symmetry of the diimine ligand, isomers or pairs of diastereomers are formed for **11**, **12**, and **6**. Additional spectroscopic details of the NMR studies can be found in Supporting Information.

■ SUMMARY AND CONCLUSIONS

In summary, Pd complexes bearing "sandwich" diimine ligands have been synthesized and explored for homo- and copolymerization reactions of ethylene and methyl acrylate. For ethylene polymerization, the catalyst resting state(s) are alkyl ethylene complex(es) and, consistent with this, the rate of chain propagation is independent of ethylene pressure. Similar polymer M_n values were obtained at varying ethylene pressures under otherwise identical reaction conditions. Notably, living polymerization of ethylene was observed at room temperature which can be attributed to the increased axial steric bulk provided by the capping arene groups. Consistent with living polymerization and increased axial bulk, the rate of associative ethylene exchange was determined to be exceedingly slow compared to other palladium diimine systems. Although the "sandwich" systems are less active than standard diimine catalyst **1**, the polyethylene produced exhibited higher branching numbers, particularly when methyl substituents are present in the diimine backbone (catalysts **3a** and **4a**, 115−117 branches per 1000 carbons). Branches on branches were observed indicating a hyperbranched polymer structure. Complexes **3a** and **3c** were also demonstrated to be effective for ethylene/MA copolymerization, yielding copolymers with reasonably narrow M_w/M_n values (1.16−1.45) in comparison to the standard diimine catalysts (1.6−1.8). Mole fractions of MA incorporation of up to 14% were achieved. Low temperature NMR mechanistic studies revealed similar features as observed for standard system **1**. Insertion of MA into the Pd−Me bonds occurs readily in a 2,1 fashion at −70 °C to yield four-membered chelates which successively isomerize to five-membered chelates and then to the most stable six-membered chelate. As for **1**, such six-membered chelates are likely catalyst resting states and retard the rate of chain growth since chelate opening and ethylene coordination is required for chain propagation.

ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs5016029.

> Synthetic procedures, polymerization methods, mechanistic studies, ^{1}H NMR spectra, and X-ray crystallographic data (PDF)

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Notes

The authors declare no competing financial interest.

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(30) The rotation barrier of ethylene was also determined using ^{1}H NMR spectral line shape analysis over a temperature range of −90 to −30 °C. The barrier ($\Delta G^{\ddagger}$) for rotation of ethylene was determined to be 9.1 ± 0.2 kcal/mol using an Eyring analysis.

(31) As noted, two isomers are observed for acrylate complex **11**. Although these could be assigned to two different rotamers of the MA π-complex, it seems more likely they are diastereomers formed by coordination of the two different enantiofaces of MA to the Pd center, which bears a C_2 symmetric diimine ligand.